Comment on "Nonlocal Van Der Waals Density Functional Made Simple"

We comment on the recent attempt [1] (VV) to simplify the construction of a van der Waals density functional. A key to the approximation was the use of arbitrarily introduced *ad hoc* Gaussian multiplicative factors (GMFs), resulting in a theory that fails badly in satisfying the law of conservation of electron number. Further criticisms, including a diverging exchange-correlation energy, are also made.

The requirement of charge-current continuity and hence charge conservation in response functions for quantum mechanical systems is embodied in what are often called f-sum rules [2], expressible as either a frequency moment of the imaginary part of the relevant response function or the high frequency limiting form of the response. We can make this simple by considering the conductivity $\sigma(q, \omega)$ of a uniform system, the current density induced by an electric field proportional to $\exp i(\mathbf{q} \cdot \mathbf{r} - \omega t)$. The high frequency response must be the same as for noninteracting electrons, $\sigma(q, \omega) = ine^2/m\omega$, independent of q, where n is the electron density. This yields a dielectric function $\epsilon(q, \omega) - 1 = 4\pi i\sigma(q, \omega)/\omega = -(4\pi e^2/m\omega^2)n$, the result obtained from the f-sum rule for this problem [2]. The sum rule or high frequency form is the same for $(1 - 1/\epsilon)$ as well as coupling constant integrated [3] versions, $\int(d\lambda/\lambda)(1 - 1/\epsilon)$.

The high frequency limit of VV's Eq. (11) is $-(4\pi e^2/m\omega^2)nF_q^2$, instead of the exact result, where the F_q factors (GMFs) would be replaced by unity. Specifically, $F_q = \exp(-Cq^2)$, where C is a function of density and spin polarization. The coefficient of ω^{-2} acts as an electron counter, where replacing n by nF_q^2 suggests that the effective number of correlating electrons is somehow dependent on q and the spin polarization. The presence of the spurious GMFs is in violation of the law of electron conservation and has a large effect on the final result, as GMFs directly multiply the residue of the only poles, which occur at a single nondispersing value of $|\omega|$.

For the nonuniform system, the error is similar. The GMFs multiplying VV's Eq. (10) violate electron conservation. They integrate to produce damping factors of the R^{-6} van der Waals interaction, which seems to imply that the mechanism for damping within this theory is that the correlating electrons simply disappear and reappear as the distance between fragments is changed. Since the integrals over q and q' diverge in the VV theory in the absence of these GMFs, the effect of electron nonconservation is clearly paramount.

VV also neglect the dependence of the excitation energies on the wave vector, which is known to exist. For example, if Eq. (11) is used in the standard expression [2] for the exchange-correlation energy of a uniform system, one obtains an infinite result, because the theory fails to produce the correct large wave-vector behavior.

The gradient expansion of the long range piece of the correlation energy set back the use of gradient expansions for years; it was large and of the wrong sign for good performance. We now know that this expansion amounted to the erroneous enterprise of attempting to expand the van der Waals interaction in gradients. Surprisingly, VV still suggest that it be done. The small q limit is singular. Singular terms of higher order than the q^2 in the energy response cause a rapid falloff [4], leaving only a tiny regime where the expansion is useful. Generalized gradient approximations typically handle the issue either by mimicking the term's rapid falloff [5], or by providing a canceling term [6] or partially canceling term [7]. The gradient coefficient of the original functional [8] becomes small (see VV, Ref. [9]) in the high density limit, where a gradient expansion might be appropriate, thus handling the issue for that functional. It is not obvious whether the VV functional handles this issue effectively.

VV criticize the integrable $R^2 \ln R$ singularity within the integrand of the final integral of our functional [8], without proof that it is incorrect. It is certainly not "harmful," nor is it reflected in the functional's expression for the pair correlation function, which itself goes to a finite constant.

Like all proper theories, the VV theory gives r^{-6} asymptotic interactions, but the damping mechanism at both short *and long* range is driven by particle nonconservation, and hence is clearly flawed, fatally in our opinion.

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